In re PATENT APPLICATION of:

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FOR: LUBRICANTS

Group Art Unit:1105

Examiner: Ogden

#35
9-26-00

DECLARATION OF RONALD PEARCE

I, Ronald Pearce, c/o Uniqema, PO Box 90, Wilton, Middlesbrough, Cleveland, TS90 8JE England do hereby solemnly and sincerely declare as follows:

1. I have the qualifications, D Phil (Chemistry) awarded by Sussex University, UK in 1969 and BSc (chemistry) also awarded by Sussex University in 1966. I was engaged in post-doctoral research at the University of Toronto in Canada in the field of organosilicone chemistry from 1969 to 1970.

2. I am presently employed as the Research and Development Manager of ICI Chemicals & Polymers Ltd (ICI) Lubricants Business, a business group within Uniqema, itself a business group within ICI. I joined the Lubricants Business in 1993 and have been R&D Manager since that time. I commenced employment with the ICI group in 1970 and have worked in various technical fields including olefin polymerisation catalysis, polyurethanes, hydroformylation, esterification, plasticisers until 1993 when I joined the Lubricants Business of ICI.

WO90/12849 (Jolley)

3. I have read and understand WO 90/12849 (Jolley) which has been cited by the Examiner against the present invention in these proceedings.

4. Jolley is concerned with liquid compositions comprising a fluorine-containing refrigerant and a lubricant of a polyol ester type. Jolley refers to hydrochlorofluorocarbon (HCFC) refrigerants and to hydrofluorocarbon (HFC) refrigerants generally and also refers specifically to HCFC 22, HCFC123, HCFC 141b, HCFC 124a, HFC 134a, HFC 23, HFC 143a, HFC 152a, HCFC 142b and HFC 134 on page 9 as examples of fluorine-containing refrigerants useful in

the compositions of Jolley. HFC 134a had been identified as a suitable replacement refrigerant for CFC 12 due to its similar physical properties.

5. The lubricants with which Jolley is concerned are defined by a general formula representing a polyol ester. The alcohol part of the ester may in essence be any alcohol having a hydrocarbyl structure with two or more hydroxyl groups. The acid part of the ester is selected from formic acid, a straight chain C_2 to C_8 acid (C_1 to C_7 alkyl), a branched chain acid or a C_9 to C_{23} acid (C_8 to C_{22} alkyl). There is a proviso that at least one of the acid groups must be formic, lower straight chain or branched chain acid or an acid group containing an acid or ester group within it. In practical terms, the proviso amounts to an exclusion from the scope of the definition of the polyol esters of only those materials in which all of the acid groups are linear and C_9 or above. In my opinion, this constitutes a definition of great breadth and, in practical terms, does not differ significantly from a definition of the polyol ester as being any polyhydroxy compound with any combination of carboxylic acids wherein the ester has a viscosity suitable for refrigeration applications.

6. As well as being miscible with the refrigerant, Jolley states on page 25 that the liquid compositions are characterised as having improved thermal and chemical stability over a wide temperature range.

7. In the examples, the synthesis of a range of lubricants is described. A selection of these lubricants are then tested for solubility with HFC 134a. No test data is presented measuring other properties of the lubricant nor with any other refrigerant. In the claims, the only specific refrigerant referred to by Jolley is HFC 134a as set out in claims 3, 11 and independent claim 18.

8. In summary, Jolley proposes HCFC or HFC refrigerants as replacements for CFCs and mentions HCFC 22 and HFC 134a specifically. HFC 134a is known to be suitable as a replacement for CFC 12 and HFC 134a is the only specific material tested and referred to in the claims. The definition of the lubricant in Jolley is very broad. The refrigerant and lubricant should be miscible and are characterised by having *inter alia* improved thermal and chemical stability.

The Present Invention

9. The present invention is concerned with identifying a replacement heat transfer fluid composition for use in systems which previously were operated using R 502 or HCFC 22, a refrigerant proposed by Jolley as a solution itself. R 502 and HCFC 22 are employed in entirely different refrigeration applications to CFC 12 and HFC 134a. This is due to the different thermodynamic characteristics of R 502 and HCFC 22 as compared to those of CFC 12 and HFC 134a. As such, the present invention addresses a technical problem in an application that Jolley does not refer to.

10. The heat transfer fluid in the present invention comprises two or more HFCs selected from HFC 32 (difluoromethane), HFC 125 (pentafluoroethane) and HFC 134a (1,1,1,2-tetrafluoroethane). Jolley does not refer either to HFC 32 or HFC 125 despite providing a list of a range of HFC refrigerants.

11. The definition of the lubricant in the present invention is limited to a polyol ester in which the alcohol is either pentaerythritol and/or dipentaerythritol. The acid is defined as being selected from a linear acid having 4 to 11 carbon atoms (3 to 10 carbon alkyl groups) and/or branched acids having 7 to 13 carbon atoms (6 to 12 carbon alkyl groups).

Experimental Data

12. A series of experiments were conducted under my supervision to repeat the procedures of Examples 1,2,6 and 11 of Jolley. The resulting products, after suitable "clean-up" to remove impurities to standards appropriate for commercial use, were then subjected to tests to assess their thermal stability, said by Jolley to be a characterising feature of his compositions. The stability of two esters falling within the definition of the lubricant in the present application was also subjected to the same tests for comparative purposes.

13. The thermal stability test is a standard industry test method (developed by ASHRAE, the American Society of Heating, Refrigeration and Air Conditioning Engineers) that is designed to mimic the more demanding conditions encountered in typical refrigeration systems. It enables the skilled worker to differentiate (screen) potential lubricants on the basis of their stability under the test conditions as measured by parameters including changes in acid value and colour which are indicative of breakdown of the lubricant. In actual operating systems, lubricant

breakdown could give rise to problems in system operability and/or operating efficiency and could potentially give rise to unpredictable system failure.

14. The esters which were tested are as follows:

- Jolley Example 1: glycerol with acetic anhydride
- Jolley Example 2: glycerol with 2-ethyl hexanoic acid
- Jolley Example 6: trimethylol propane with C8C10 methyl-ester and acetic anhydride
- Jolley Example 11: pentaerythritol with C8C10 methyl-ester and acetic anhydride.
- ISO 22 ester: pentaerythritol with linear acids in C_5 to C_{10} range
- ISO 32 ester: pentaerythritol with linear and branched acids in C_5 to C_{10} Range

14. Prior to being subjected to the test procedure set out below, the total acid number, viscosity (using a Brookfield kinematic viscometer), moisture content and the colour (in Hazen units) of the lubricants were determined. The results are as follows for the viscosity and moisture with the acid number and colour results being shown in paragraph 15 with the end results for comparison:

	ISO 22 Ester	ISO 32 Ester	Example 1 of Jolley	Example 2 of Jolley	Example 6 of Jolley	Example 11 of Jollley
Moisture (ppmw/w)	16	43	45	16	24	36
Viscosity (cPs)	19.5	30.7	8.7	24.6	18.3	45.1

15. The tests were carried out in duplicate on each ester in clean, dry 300 ml autoclaves. About 40g of the lubricant was placed in the autoclaves with standard test metal pieces of Al, Cu, Fe, sealed and evacuated. About 35g of refrigerant 407C, a ternary blend of HFC32, HFC125 and HFC 134a in a ratio of 23:25:52, was then charged to the autoclaves. The autoclaves were heated to and maintained at a temperature of about 175 C and a pressure of about 600psig in the presence of the gaseous refrigerant blend. The tests were carried out for a period of 14 days after which the lubricant was degassed and subjected to measurements to determine total acid number and the colour and visual inspection. The results are shown below:

Lubricant	Acid Value mgKOH/g		Colour Hazen units		Other
	Start	End	Start	End	
Eg 1 (Run 1)	0.03	0.45	10	50	-
Eg 1 (Run 2)	0.03	0.47	10	50	-
Eg 2 (Run 1)	0.06	18.5	40	>250	White particles in lubricant
Eg 2 (Run 2)	0.06	15.3	40	>250	White particles in lubricant
Eg 6 (Run 1)	0.01	0.29	10	60	-
Eg 6 (Run 2)	0.01	0.65	10	80	-
Eg 11 (Run 1)	0.04	0.94	30	70	Cloudy white emulsion suspended throughout
Eg 11 (Run 2)	0.04	1.67	30	80	Cloudy white emulsion suspended throughout
ISO 32 (Run 1)	0.03	0.09	20	40	-
ISO 32 (Run 2)	0.03	0.11	20	50	-
ISO 22 (Run 1)	0.02	0.08	20	40	-
ISO 22 (Run 2)	0.02	Test leaked	20	Test leaked	Test leaked

16. The tests results illustrate that ISO 22 and ISO 32 esters, within the scope of the definition of the lubricant in the present application exhibit acceptable increases in total acid number and in colour change during the stability testing with R407C. Furthermore, these esters do not show the large increase in acid number shown by Examples 1, 2, 6 and 11 of Jolley and the esters show at least comparable if not superior colour results as compared thereto.

17. In particular, as compared to Example 1, the total acid number of ISO 22 and ISO 32 increased to about 0.10 whereas for Examples 1, 6 and 11 the increase from a similar starting value was much greater, being to about 0.46, 0.29 or more and 0.94 or more respectively, with Example 2 being comparatively of very poor stability. The colour data was at least comparable with if not superior to that of Examples 1, 2, 6 and 11.

18. Example 11 was derived from a pentaerythritol ester. As shown in the table in paragraph 15, under the test regime this ester gave rise to a cloudy appearance, in contrast to the

pentaerythritol esters of the subject invention, thus illustrating the improved stability of esters having acid groups as defined in the present invention.

19. In conclusion, the esters of the present invention when subjected to stability testing with a refrigerant blend show greater stability than the esters of Examples 1, 2, 6 and 11 of Jolley. In addition, taking account of the lack of reference in Jolley to refrigerant blends or to two of the specific HFC's recited in the claims of the present application along with the breadth of the disclosure of the lubricant in Jolley, I conclude that the teaching of Jolley would not lead a person skilled in the art to the present invention.

20. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that wilful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such wilful false statements may jeopardise the validity of the application or any patent issued thereon.

Ronald Pearce

Ronald Pearce Date 04/09/00 (4th Sept 2000)